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The Heck Reaction of Benzo[*b*]thiophene[1)]

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Abstract.

Arylpalladium chloride, prepared *in situ* arylmercuric chloride and lithium chloropalladite, reacts with benzo[*b*]thiophene to produce 2- and 3-arylbenzo[*b*]-thiophenes, accompanied by a significant amount of biaryl. On the other hand, in the presence of palladium acetate, benzo[*b*]thiophene reacts with styrene to produce 2- and 3-styrylbenzo[*b*]thiophenes.

Introduction.

The reactions of olefins in the presence of transition metal compounds have been studied by many workers.[2)] Recently, the arylation of olefins with arylpalladium compounds, formed *in situ* by the exchange of arylmercuric compounds with Group VIII metal salts, has been shown to be a useful reaction for the synthesis of various olefinic compounds.[3),4)] We have previously reported[5)] that the Heck reaction of benzo[*b*] furan with arylpalladium chloride (**1**) led to the formation of 2-arylbenzo[*b*]furan derivatives, whereas in the presence of palladium(II) acetate the reaction of benzo[*b*]furan with olefins produced 2-benzo[*b*]furyl-substituted olefins accompanied by a small amount of 2,2-bibenzo[*b*]furyl. In order to study whether or not the Heck arylation occurs in the reaction of benzo[*b*]thiophene (**2**) with **1**, the reaction of **2** with arylmercuric compounds was performed in the presence of palladium(II) salts. This report also contains the results of a study of the reaction of **2** and styrene in the presence of palladium(II) acetate.

Results and Discussion

In the presence of lithium chloropalladite, the reaction between **2** and phenylmercuric acetate in ethanol at room temperature gave 2-phenylbenzo[*b*]thiophene (**3-a**), 3-phenylbenzo[*b*]thiophene (**4-a**), and biphenyl (**5-a**) in yields of 4%, 13%, and

42%, respectively. The result of the reaction is summarized in Table I. Heck[3,4] and Henry[6] independently described that the Heck reaction generally proceeds *via* a *cis* arylpalladation to olefinic double bond followed by a *cis* elimination of a hydride palladium(II) species, and Heck[3] moreover suggested that, if a *cis* hydride elimination are not possible, a *trans* palladium(II)-hydride elimination can occur. In the reaction of 2 and 1, since the aryl group is covalently bonded to palladium(II), arylpalladation would be expected to be a *cis* process, then the arylation of 2 is considered to proceed *via* a *cis* arylpalladation followed by a *trans* hydrido-palladium(II) elimination. Furthermore, making a sharp contrast to case of benzo[*b*]furan with 1, 2 undergoes arylation reaction only in 17% yield the major reaction is a coupling reaction of the arylating agent to form biaryls. In addition, with 2, arylation reaction took place at both of 2- and 3-position, whereas benzo[*b*]furan was arylated only at the 2-positin. These results indicate that the reactivity of 2 towards 1 is much lower than that of benzo[*b*]furan, and 1 reacts with itself faster than 2.

Recently, Moritani et al.[7] reported that the reaction of thiophene and styrene in the presence of palladium acetate resulted in the formation of *trans*-2-styrylthiophene and *trans,trans*-2,5-distyrylthiophene. We also reported that the reaction of benzo[*b*]furan and styrene resulted in the formation of 2-styrylbenzo[*b*]furan (69%), accompanied by 2,2'-bibenzo[*b*]furyl (7%).[5] When a solution of 2 and styrene in acetic acid was heated under reflux in the presence of palladium(II) acetate, 2-styrylbenzo[*b*]thiophene (**6**) (49%) and 3-styrylbenzo[*b*]thiophene (**7**) (9%) were obtained as the products. The formation of 6 and 7 is considered to proceed *via* a palladation of 2 with palladium(II)acetate, followed by a *cis* addition benzo[*b*]thienylpalladium(II) species to olefinic double bond and a *cis* hydrido-palladium(II) elimination. In general, nitration, halogenation, chloromethylation, acetylation and mercuration of 2 all give predominantly the 3-isomer.[8] On the other hand, metallation of 2 with *n*-butyllithium occurs almost quantitatively at 2-position.[9] The result of the reaction of 2 with styrene indicates that the reactivity of 2 is lower towards palladium(II) acetate than that of benzo[*b*]furan, and also that the palladation reaction of 2 with palladium(II) acetate occurs mainly at 2-position as well as the metallation of 2 with *n*-butyllithium.

Experimental

Materials. All melting points and boiling points are uncorrected.

The palladium(II) acetate was prepared according to the procedure of Wilkinson.[10] The following compounds were synthesized by the methods described in the literature: *p*-tolylmercuric chloride,[11] *p*-anisylmercuric chloride.[12] The phenylmercuric acetate and the starting benzo[*b*]thiophene were of commercial grade.

The Arylation of Benzo[b]thiophene (2). A lithium chloropalladite solution was

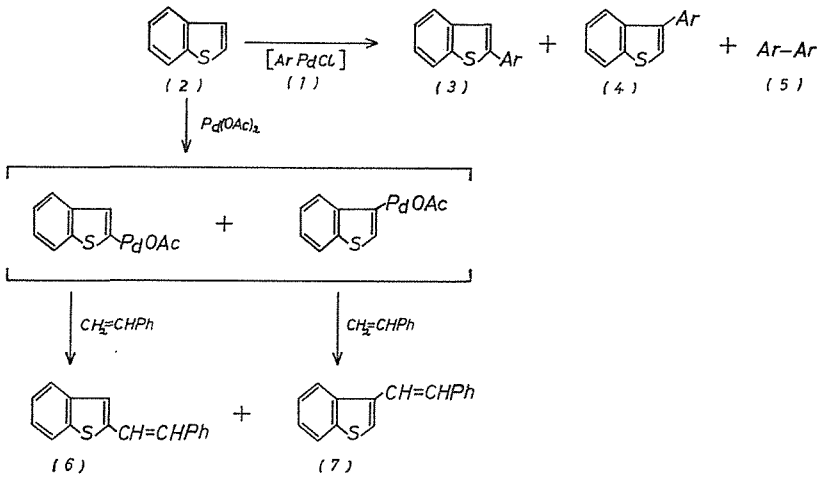

Fig. I.

prepared by stirring 0.84 g (0.02 mol) of anhydrous lithium chloride and 1.77 g (0.01 mol) of palladium(II) chloride overnight at room temperature in 80 ml of ethanol. To this lithium chloropalladite solution, a mixture of 0.01 mol of aryl mercuric compound and 0.02 mol of 2 was added and then was stirred at room temperature for 12hr. The products were isolated by filtrating precipitated palladium and then distilling the solvent under reduced pressure. Analyses of the reaction products were usually made by gas chromatograpy on a 1 m of SE 30 (15%) on chromosorb w column using Hitachi K-53 gas chromatograph. As internal standard, 2 mmol of *n*-dodecane was added to the reaction mixture. The products were identified by comparing the retention times and, when necessary, by the mixed-melting-point-determination with those of authentic samples after separation by preparative gas chromatography. These results are summarized in Table I.

The Reaction of Benzo[b]thiophene (2) *with Styrene.* A mixture of palladium(II) acetate (10 mmol), styrene (10 mmol), and 2 (10 mmol) was stirred in acetic acid (100 ml) for 6 hr under reflux. The resulting mixture was filtered to remove palladium metal, and, after the evaporation of the solvent under reduced pressure, the residue was poured into water. The organic layer was extracted with ether, treated with an aqueous sodium bicarbonate solution, washed with water, and then dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the products were isolated by column chromatography. The first elution with benzene afforded oil which was identified as the unreacted 2 (17%) by comparing the retention times of gas chromatography and IR and NMR spectra with those of the authetic sample.

The second elution with benzene afforded the 2-styrylbenzo[*b*]thiophene (**6**), bp 134-136°C/0.1 mm Hg, in 9% yield. The structure of **6** was confirmed by IR spectrum and by the fact that hydrogenation with Raney-nickel resulted in the

formation of 1,4-diphenylbutane (mp 52°C). IR spectrum: 965, 750, 740, and 690 cm^{-1}. Found: C, 81.40; H, 5.38%. Calcd. for $C_{16}H_{12}S$: C, 81.35; H, 5.08%.

Further elution with benzene and recrystallization from ethanol afforded colorless crystals which were identified as 3-styrylbenzo[*b*]thiophene (**7**), (mp 96-97°C, yield 49%, lit.[14] mp 97°C).

Table I. **The Arylation of Benzo[*b*]thiophene (2) with Arylpalladium Compounds(1).**

Arylating Agent	Products	Yield s%[a]
Phenylmercuric acetate	2-Phenylbenzo[*b*]thiophene (**3-a**)[b]	4
	3-Phenylbenzo[*b*]thiophene (**4-a**)[c]	13
	Biphenyl (**5-a**)[d]	42
p-Tolylmercuric chloride	2-*p*-Tolylbenzo[*b*]thiopnene (**3-b**)[e]	3.5
	3-*p*-Tolylbenzo[*b*]thiophene (**4-b**)[f]	12.5
	Bi-*p*-tolyl (**5-b**)[g]	42
p-Anisylmercuric chloride	2-*p*-Anisylbenzo[*b*]thiophene (**3-c**)[h]	3
	3-*p*-Anisylbenzo[*b*]thiophene (**4-c**)[i]	10
	Bi-*p*-anisyl (**5-c**)[j]	45

a) Yields are based upon the arylating agent.

b) Mp 174-175°C, (lit.[k] mp 174-175°C).

c) Bp 8-589°C/0.1mm Hg, (lit.[k] bp 75-90°C/0.1mm Hg).

d) Mp 68-69°C, (lit.[l] mp 69-70°C).

e) Mp 181-182°C, (the authentic sample (mp 181-182°C) was synthesized from phenyl-4-methylphenacylsulfide by a modification of Dann's procedure.[k]).

f) Bp 110-112°C/0.1mm Hg, (the authentic sample (bp 108-110°C/0.1mm Hg) was synthesized from phenyl-4-methylphenacylsulfide by a modification of Dann's procedure[k]).

g) Mp 119-120°C, (lit.[m] mp 120°C).

h) Mp 194-195°C, (lit.[n] mp 193-194°C).

i) Mp 110-111°C, (the authentic sample, mp 110°C, was synthesized from phenyl-4-methoxyphenacylsulfide by a modification of Dann's procedure[k]).

j) Mp 170-171°C, (lit.[m] mp 170-172°C).

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ベンゾ〔b〕チオフエンの Heck の反応

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アルコール中塩化アリール水銀と塩化パラジウム酸リチウムより作ったアリールパラジウムクロラクドをベンゾ[*q*]チオフエント反応させ，2-フエニルベンゾ[*b*]チオフエン，3-フエニルベンゾ[*b*]チオフエンおよびビフエニルをそれぞれ4%，13%，42%の収率でえた。また酢酸中，酢酸パラジウムの存在でベンゾ[*b*]チオフエンとスチレンを反応させると，2-スチリルベンゾ[*b*]チオフエン，3-スチリルベンゾ[*b*]チオフエンをそれぞれ49%，13%の収率でえた。